

Contribution to Electroreduction of Hydrazones  
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To contribute to the understanding of the limited extent of conjugation in compounds containing grouping  $C=N-N=C$  (1), the electroreduction and hydrolysis of azines of the type  $ArCH=N-N=CHAr$  was studied (2). For this purpose, it was essential to understand in more detail the electrochemical behaviour of hydrazones. Similarly, such information was important for investigation of the mechanism of the addition of the protonated form of hydrazine to benzaldehydes (3).

A protonated form of common hydrazones derived from aromatic aldehydes or ketones is usually reduced in a single four-electron step. It has been proved (4) that in this process a two-electron cleavage of the N-N bond occurs first, followed by a two-electron reduction of the resulting imine. As the hydrogenation of the azomethine bond in the imine usually occurs at a potential either similar or more positive than the reductive cleavage of the N-N bond, a single four-electron wave results.

To decide, where the protonation of the hydrazone occurs, the reduction of two N,N,N-trialkylammonium derivatives - of benzaldehyde and acetophenone - was investigated. The reduction of these compounds of the type  $ArC(R')=N-NR_3^+$  occurs over the entire pH range in two two-electron steps, with potentials differing by about 0.1V. The pH-dependence of half-wave potentials indicate a surface protonation, preceding the first electron uptake. The reduction thus involves a species with two positive charges on two adjacent nitrogen atoms. We are aware

that existence of species bearing two positive charges on two adjacent atoms is considered doubtful by organic chemists, but the experimental evidence for the existence of such reactive species at the electrode surface is conclusive.

The above conclusion is supported by the behaviour of benzaldehyde hydrazones, which bear no substituent of nitrogen. Dependence of half-wave potentials and limiting currents of these compounds indicate, that the reduction is accompanied by two acid-base equilibria. The diprotonated form is reduced in acidic media in a single four-electron step. In the medium pH-range, where the surface protonation is not sufficiently fast to generate the diprotonated form, formation of a monoprotated form predominates. The monoprotated form is reduced in a two-electron step, producing a hydrazine derivative. This resembles the reduction of some oximes (5), which in slightly basic media are reduced to hydroxylamine

derivatives. The unprotonated form of studied hydrazones is not reduced in protic media within the available potential range.

The hydrogenation of the azomethine bond in the medium pH range indicates that the site of the hydrogen ion in the monoprotated form is preferably on the nitrogen of the azomethine bond. > Hydrolysis of the N,N,N-trimethylhydrazinium derivatives of benzaldehyde and acetophenone is currently studied in alkaline media to distinguish between specific basic and nucleophilic catalysis.

#### References

- (1) P.Zuman; J.Ludvik, *Tetrahedron Lett.* 2000, 41, 7851.
- (2) D.Rozbroj, J.Ludvik, unpublished results.
- (3) M.S.Baymak, unpublished results.
- (4) H.Lund, *Acta Chem.Scand.* 1959, 13, 349, 1964,18,563.
- (5) H.Lund, *Tetrahedron Lett.* 1968, 3651.